

A SIMPLE DEVICE FOR THE COLLECTION OF WATER AND DISSOLVED GASES AT DEFINED DEPTHS

J. H. Loughrin, C. C. Bolster, N. C. Lovanh, K. R. Sistani

ABSTRACT. A device, consisting of a jar fitted with an inlet comprised of a gas-tight check valve and two-way ball valve outlet connected via tubing to a portable peristaltic pump, was constructed to collect water samples without atmospheric contamination or loss of dissolved gases. A headspace void for dissolved gas analysis was created by enclosing silicone tubing sealed with rubber stoppers within the jar. The device was deployed in a 0.4-ha lagoon that served as the primary waste recipient of a 2,000-sow farrowing operation as well as a 4,000-ha impoundment reservoir. Water samples were analyzed for dissolved methane and common indices of water quality such as pH, suspended solids, various ions, and metals concentration. In addition, lagoon wastewater samples were analyzed for malodorous compounds. For reservoir samples, methane concentrations at the bottom of the lake of $60 \mu\text{g L}^{-1}$ were about three orders of magnitude higher than at the upper levels of the lake while ammonium levels increased from 0.03 mg L^{-1} at the surface to 1.67 mg L^{-1} in bottom samples. pH steadily decreased from 8.58 near the surface to 7.47 at the bottom. Other water quality parameters such as dissolved metals were similar at each depth. For lagoon samples, ammonium concentration and malodorous compounds declined markedly as temperatures warmed. Results for both reservoir and lagoon sampling indicate that this device affords an inexpensive yet effective means of water collection for subsequent analysis of both water quality and dissolved gas concentration.

Keywords. Depth, Lagoons, Lake, Odor, VOC, Wastewater, Water, Water quality.

There are a number of means available for the collection of environmental water samples prior to analysis. Most often, samples are simply collected in suitably cleaned jars and transported to the laboratory. Analysis of dissolved gases such as O_2 is done in the field using a special oxygen sensor if required. In other instances, however, a more thorough analysis of dissolved gases is required. Methane, H_2 , CO_2 , N_2 , and even noble gases (Spaulding and Watson, 2006; Cey et al. 2008) may be of interest in some situations.

A number of devices have been developed for collection of submerged water samples and the analysis of dissolved gases. Often, special vessels for the collection of submerged water samples are quite expensive. The Nansen jar (Warren, 2008), for instance, is used to sample water at great depths such as in the ocean. These vessels are lowered on a special line and inverted for water sample retrieval when a weight is

dropped down the line to tip the bottle. A more recent version of the Nansen jar, the Niskin bottle, uses either weight-activated springs or pressure-actuated valves to open and close the bottle (Liu et al., 2005). While these vessels afford collection of samples at various depths, there is no provision for preventing loss of dissolved gases or atmospheric contamination of the water when the vessels are opened to retrieve water. Such bottles have been shown to have significant losses of dissolved O_2 from the time at which the sample is collected and the bottle is retrieved (Worthington, 1982).

A pump may also be used to draw water from well-defined depths (Liu et al. 2005; Strady et al., 2008) and transferred to sample bottles, but again, there is usually no provision for preventing the loss of dissolved gases. In this case, and in the case of submerged sampling jars, while water analyses can be performed, dissolved gases may be lost.

Other devices, such as that of Spaulding and Watson (2006), allow for measurement of dissolved gas but not for other water quality analyses. In certain situations, it is desirable that samples collected for dissolved gas analysis can be used for other water quality analyses.

In 1990, Holter published a technique for monitoring greenhouse gases in soil using silicone tubing. This tubing had an advantage over previous techniques in that the gas sample could not be contaminated by penetration of soil or water into the sampler although the silicone tubing was very permeable to gases. Later, Jacinthe and Dick (1996) used silicone tubing to sample nitrous oxide in waterlogged anoxic soils. They found N_2O equilibrated in less than 5 h across a 2.4-mm thick non-reinforced silicone wall at 22°C . Spaulding and Watson (2006) showed that H_2 and He equilibrated across their silicone tubing within 12 h of immersion. These

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samplers, however, were field-deployed and therefore no water quality analysis could be performed using the same sample under the same set of conditions.

We envisioned a device in which water samples could be collected with gas-tight jars to prevent atmospheric contamination of samples and loss of sampled gases. With this in mind, we fashioned a vessel out of a jar fitted with gas-tight two-way ball and check valves to serve as the vessel's outlet and inlet, respectively. A piece of silicone tubing, such as that employed by Jacinthe and Dick (1996), served as a headspace void for dissolved gas analysis. Using this simple device, a water sample is drawn into the jar and, once suction to the jar is ceased, dissolved gas loss is eliminated by closure of the check valve and the pressure that remains on the outlet of the jar until the two-way ball valve is closed. This article reports the use of the device to sample water quality and dissolved gases in natural water and wastewater samples.

MATERIAL AND METHODS

WATER SAMPLING APPARATUS

The sampling jars were constructed from 1-pint (473-mL) Mason-style canning jars (fig. 1). The top of the lids were reinforced with 6.4-mm thick Plexiglas disks fitted with a two-way ball valve and a gas-tight check valve with Viton seals (US Plastic Corp., Lima, Ohio) so that flow into the jars came through the check valve and exited through the ball valve. An empty 12-cm long piece of silicone tubing (US Plastic Corp.) with an inner diameter of 1.27 cm (0.5 in.) closed at both ends with red rubber stoppers (Thermo Fisher Scientific, Waltham, Mass.) was placed in the jar. Before sampling, the jars were completely filled with water to facilitate their sinking and to prevent degassing of water samples when suction was applied.

In preliminary experiments, the time required to purge the jars of their water and replace it with environmental samples was determined by placing two drops of FDA Blue 1 dye in jars filled with tap water. The jars were connected to the peristaltic tubing and submerged in a water trough filled with tap water. Water was drawn through the jars for 30, 60, 90, 120, or 180 s and the relative amount of dye remaining was determined by reading absorbance at 610 nm. This experiment was performed three times.



Figure 1. Water sampling device. 1. Gas-tight check valve; 2. Two-way ball valve; 3. Silicone tubing closed with rubber stoppers.

GAS EQUILIBRATION TIME

The time required for methane to equilibrate across the silicone tubing was determined by pumping water from a small swine waste lagoon located on the Western Kentucky University farm into jars setup as previously described and withdrawing gas samples from the silicone tubing at 1-h intervals from 0 to 8 h and analyzing gas composition as described below. Ambient air served as time zero samples. These experiments were repeated three times.

SITE DESCRIPTIONS AND SAMPLE COLLECTION

The first site was a 0.4-ha lagoon that served as the primary waste treatment/containment structure of an approximately 2,000-sow farrowing operation. Waste was drained into the lagoon from each of the five swine houses once weekly from a pit underneath the slatted floor of the housing. The pits were then refilled as waste accumulated under the slatted floors. No pit-recharge from the lagoon was employed. Samples were taken every one to two weeks from 25 March to 2 July 2008 and then monthly thereafter. Five samples each were taken at a depth of 0.3 and 0.9 m.

The second sampling site was at Barren River Lake, an approximately 4,000-ha man-made impoundment reservoir of the Barren River in southern Kentucky. The lake has a maximum depth of 36 m and an average channel depth of 19 m at full winter pool (elevation 160 m). On the date of sampling, the pool level was 165 m. The lake is surrounded by low wooded hills and ridges and has a maximum width of 388 m.

Samples were taken in the main channel near the lake's dam on 22 August 2008. Samples were taken near the surface (0.3 m deep), at 4.6 and 6.1 m deep and at the lake bottom at depths ranging from 13.4 to 14.9 m. The samples taken at the two intermediate depths were taken since data from the U.S. Army Corps of Engineers (<http://www.lrl.usace.army.mil/wc/wq/brtext.html>) indicated that this was the approximate depth of the lake's thermocline. Triplicate samples were taken at each depth.

In the case of both lake and waste lagoon sampling, the two-way ball valve was connected to 12.5-mm diameter peristaltic tubing and Masterflex E/S portable peristaltic pump with a nominal maximum pump rate of 1,140 mL min⁻¹ (Cole-Palmer, Vernon Hills, Ill.). The sampler was submerged and water was pumped for 5 min. The peristaltic tubing was then clamped to retain pressure in the peristaltic tubing, the pump was turned off, and the sampler retrieved. The two-way ball valve was then closed to retain sampled gases in the jar before removal of the peristaltic tubing.

The jars were kept in a cooler before transport to the laboratory. They were then placed in a refrigerator at 4°C overnight to allow for gas equilibration across the silicone tubing (see following sections). The next day, the jars were removed and warmed to room temperature, and 1-mL gas samples were withdrawn from the silicone tubing for gas analysis and water samples were taken for solids, odor, and Inductively Coupled Plasma (ICP) analysis as described.

METHANE ANALYSIS

Twenty-mL headspace vials were flushed with high-purity He at approximately 140 Pa by means of a gas inlet and outlet constructed from luer-lock syringe needles piercing the vial's rubber septum. A 0.5-mL sample was withdrawn

from the vials and replaced with 1.0 mL of the sampler headspace.

Methane was analyzed on a Varian Model CP-3800 (Varian Associates., Palo Alto, Calif.) gas chromatograph (GC) equipped with a model 1041 on-column injector operated at 75°C and 263 kPa which was connected to a Silcosteel gas sampling loop with a 10-position switching solenoid valve. Five mL of sample headspace was injected using a syringe temperature of 35°C and syringe flush time of 30 s with 250 µL of the sample transferred onto a 1.8 m by 1.6 cm o.d. column packed with 80/100 mesh HayeSep Q (Varian Associates) with a flow rate of 55 mL min⁻¹. The column was connected to a flame ionization detector (FID) operated under the following conditions: N₂ makeup gas 15 mL min⁻¹, H₂ 30 mL min⁻¹, air 300 mL min⁻¹. The gas sample loop was back-flushed for 2 min after sample injection. Quantification was performed relative to a 5,000 µg L⁻¹ volume standard of CH₄ in N₂ which was run before and after each batch of samples in the case of wastewater samples and a 5 µg L⁻¹ standard of CH₄ in N₂ for reservoir water analysis.

Dissolved CH₄ concentration in the water samples was calculated by equation 1 given in Jacinthe and Groffman (2001) for a silicone tubing-based dissolved gas sampler:

$$[X]_{aq} = \left(\frac{[X]_g M_w}{HRT} \right) \left(\frac{1 \dots \text{atm}}{10^6 \mu\text{L} \dots \text{L}^{-1}} \right) + \left(\frac{[X]_g V_g \rho}{V_w} \right) \quad (1)$$

where $[X]_{aq}$ = the concentration of CH₄ in solution, $[X]_g$ is the concentration of CH₄ in the silicone tubing (µL L⁻¹, v v⁻¹), M_w is the molecular weight of CH₄ in mg mol⁻¹, H is the dimensionless Henry's constant for CH₄ (27.02, Howard and Meylan, 1997), R is the universal gas constant (8.205 × 10⁻² L atm K⁻¹ mol⁻¹), T is the temperature in degrees Kelvin (295°K), ρ is the density of CH₄ (7.07 × 10⁻⁴ mg µL⁻¹), and V_w and V_g are the volumes of the water in the sampling vessel and the headspace within the silicone tubing (L).

ODOR ANALYSIS

For odor analyses, Twisters stir bars (10 × 3.2 mm; Gerstel, Baltimore, Md.) with a 1-mm polydimethylsiloxane (PDMS) coating were preconditioned for 1 h at 250°C under a stream of high purity N₂. Ten-milliliter swine lagoon samples were placed in 20-mL glass vials closed with Teflon-lined caps along with the Twister extractors; the vials were then closed, and the samples extracted from 1 h at 500 rpm in room temperature. Afterwards, the Twisters were removed from the vials, rinsed with deionized water, blotted dry and placed in 17.8 cm long × 4-mm internal diameter thermal desorption tubes (Supelco Inc., Bellefonte, Pa.) and desorbed in a model TDSA thermal desorption system (Gerstel). Retained compounds were desorbed using an initial temperature of 25°C with a delay time of 0.25 min and then heated at 60°C min⁻¹ to 225°C with a final time of 3 min. Desorbed volatiles were transferred by a heated transfer line maintained at 240°C to a glass wool packed injection liner maintained at 50°C with liquid CO₂. Retained compounds were then transferred with a 20:1 split ratio to a 30 m × 0.25 mm VF-23MS column (Varian Associates) with a film thickness of 0.25 µm by heating the injector at 10°C min⁻¹ to 300°C with a final time of 3 min. Gas chromatography-mass spectroscopy (GC-MS) was performed on a Varian

Saturn 2000 ion trap interfaced to a Varian model 3800 GC (Varian Associates). GC operating conditions were: He carrier constant flow rate of 1 mL min⁻¹, column oven 55°C for 1 min, then programmed at 7°C min⁻¹ to 100°C, and hence at 15°C min⁻¹ to 295°C and held for 10 min, transfer line temperature 300°C. The mass spectrometer was run in electron ionization mode with an emission current of 10 m amperes using a scan time of 0.35 s and a scan range of 45 to 225 atomic mass units. All compounds were quantified by means of an external standard calibration curve developed with authentic samples of compounds (Sigma Aldrich, St. Louis, Mo.).

EFFECT OF SILICONE TUBING ON ODOR COMPOUND ANALYSIS

The effect of the silicone tubing on odor compound quantification was determined by incubating samples of swine waste slurry in sampling jars with and without added silicone hosing as used for gas equilibration studies. The slurry samples were incubated overnight after which samples were removed for analysis as described above. This experiment was replicated six times.

WATER QUALITY ANALYSIS

ICP analysis of Fe, Si, Al, and S was performed on a Varian Vista-Pro ICP-OES after microwave digestion of a sample at 175°C for 10 min. Ion chromatography of NH₄⁺, PO₄⁻, NO₃⁻, NO₂⁻, Cl⁻, and SO₄⁻ was performed on a Dionex ICS 3000 ion chromatograph (Dionex Corp., San Francisco, Calif.). Seven-mL samples were filtered through 0.2-µm filters and 25-µL samples were injected. For anion analyses, AS22 Eluent Reagent (Dionex Corp.) was pumped at 1 mL min⁻¹ through a 250- × 4.0-mm IS22 column equipped with a 50 × 4.0 mm IonPac AG22 guard column (Dionex Corp.) to a conductivity detector held at 25°C and equipped with an anion self-regenerating suppressor. For cation analyses, 20 mM methanesulfonic acid was pumped at 1.2 mL min⁻¹ through a 250- × 4.0-mm IonPac CG12A column equipped with a 50- × 4-mm CG12A guard column and hence to a cation ion detector held at 25°C and equipped with a cation self-regenerating suppressor. Chemical oxygen demand (COD) was determined using dichromate reactor digestion kit for high strength wastewater (Chemetrics Inc., Calverton, Va.). One mL samples were digested for 2 h at 150°C and after the samples cooled, absorbance was read at 620 nm. Total suspended solids (TSS) were determined according to Standard Method 2540 E (APHA, 1998). TSS were that portion of solids retained on a glass microfiber filter with a nominal pore size of 1.5 µm (Whatman grade 934-AH; Whatman, Clifton, N.J.) after filtration and drying to constant weight at 105°C.

RESULTS AND DISCUSSION

JAR PURGE TIME

Although we could have assumed a minimum time necessary to completely purge the jars of their original contents and replace them with environmental samples, we determined this value directly by placing a dye solution in the jar and pumping at the same rate as for environmental samples. By approximately 72 s, only about 1% of the dye remained in the jars confirming that 5 min was more than

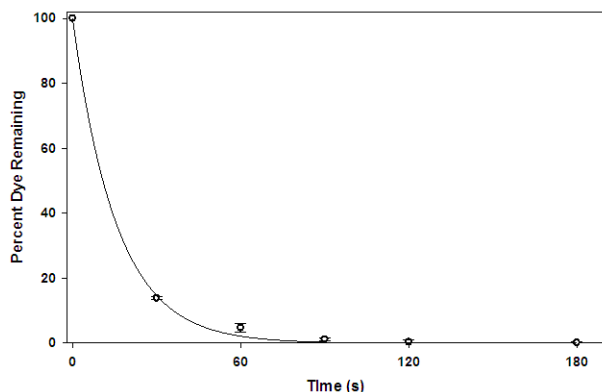


Figure 2. Results of dye test to determine time required to completely purge sampling jars. Data represent the mean of three determinations \pm standard deviation.

sufficient to completely purge the jars of all water and dissolved gases (fig. 2).

GAS EQUILIBRATION TIME

Probable equilibration time was less than 8 h for methane (fig. 3). This indicated that equilibrium with the environment was achieved fairly rapidly and that storing the sampling jars overnight before analyses would not induce bias because of premature removal of the tubing that served as the sampler's headspace.

RESERVOIR SAMPLES

The Barren River Lake reservoir is a large narrow impoundment surrounded by low hills. As such, the fetch length is limited and there is limited energy available to prevent thermal stratification occurring during the summer.

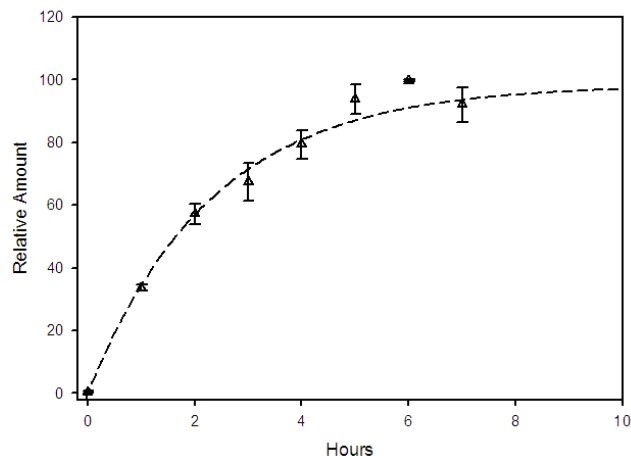


Figure 3. Time to achieve equilibrium in sampling jars for methane. Data represent the mean of three determinations \pm standard error.

The lake was chosen as a sampling site for this reason to increase the probability that clear differences in water chemistry related to depth would be obtained.

Table 1 presents solids, elemental and ionic analyses of the lake samples. While the differences due to depth in the concentration of most analytes were small, some of these were significant. pH declined steadily from 8.58 at the lake's surface to 7.47 at the bottom of the lake. Suspended solids, turbidity, calcium, manganese, ortho-phosphate, and silicon all occurred in higher concentrations near the bottom of the lake than near the surface. No differences due to depth were seen for chloride, total phosphorus, sodium, or potassium. Interestingly, both total sulfur and sulfate were lower at the bottom of the lake than at lesser depths.

Table 1. Analysis of water samples obtained at Barren River Lake reservoir.^[a]

Parameter	Depth			
	Lake Surface	4.6 m	6.1 m	Lake Bottom
pH	8.58 \pm 0.10 b	8.35 \pm 0.11 b	7.99 \pm 0.179 b	7.47 \pm 0.14 a
Suspended solids (mg L ⁻¹)	2.14 \pm 0.89 b	2.43 \pm 0.86 b	1.93 \pm 0.96 b	4.29 \pm 1.06 a
ortho-Phosphate (μ g L ⁻¹)	20.9 \pm 4.98 b	15.6 \pm 2.04 b	56.1 \pm 40.3 ab	112 \pm 24.6 a
Turbidity (mg L ⁻¹)	1.85 \pm 0.14 b	2.04 \pm 0.25 b	3.01 \pm 0.63 b	7.82 \pm 1.42 a
Ion Analysis				
Sulfate (mg L ⁻¹)	12.1 \pm 0.48 a	12.4 \pm 0.63 a	12.3 \pm 0.81 a	8.1 \pm 0.58 b
Chloride (mg L ⁻¹)	8.39 \pm 1.32 a	6.59 \pm 0.38 a	6.82 \pm 0.45 a	6.35 \pm 0.25 a
ICP Analysis				
Phosphorus (μ g L ⁻¹)	20.9 \pm 4.98 a	15.6 \pm 2.08 a	112 \pm 24.6 a	85.9 \pm 23.1 a
Sulfur (mg L ⁻¹)	3.87 \pm 0.17 a	3.67 \pm 0.11 a	3.65 \pm 0.10 a	2.33 \pm 0.19 b
Iron (μ g L ⁻¹)	0.80 \pm 0.41 a	1.30 \pm 0.84 a	7.27 \pm 6.16 a	5.89 \pm 2.82 a
Manganese (μ g L ⁻¹)	0.77 \pm 0.34 b	-- ^[b]	0.72 \pm 0.38 b	830 \pm 289 a
Magnesium (mg L ⁻¹)	6.30 \pm 0.08 a	6.59 \pm 0.07 a	6.39 \pm 0.07 a	6.29 \pm 0.02 a
Aluminum (μ g L ⁻¹)	6.19 \pm 1.03 a	5.67 \pm 1.08 a	8.67 \pm 4.85 a	3.26 \pm 1.06 a
Sodium (mg L ⁻¹)	3.43 \pm 0.21 a	3.03 \pm 0.20 a	2.85 \pm 0.16 a	2.91 \pm 0.21 a
Potassium (mg L ⁻¹)	5.13 \pm 1.78 a	2.35 \pm 0.11 a	4.13 \pm 0.63 a	2.38 \pm 0.08 a
Calcium (mg L ⁻¹)	25.7 \pm 0.64 c	27.8 \pm 0.11 b	26.7 \pm 0.40 bc	31.9 \pm 1.44 a
Silicon (mg L ⁻¹)	0.49 \pm 0.044 b	0.50 \pm 0.049 b	0.63 \pm 0.042 b	2.24 \pm 0.25 a

^[a] Data represent the mean of six determinations \pm standard error of the mean. Within rows, means followed by the same letter are not significantly different by a least significant difference test at $\alpha=0.05$.

^[b] Below limit of detection.

It is also interesting to note that of detected metals, only manganese and calcium occurred in significantly higher concentrations at the bottom of the lake than at shallower depths. It is likely that the pH at the bottom of the lake, while still above 7.0, favored some dissolution of manganese from the lake sediment thereby increasing the manganese concentration in the water. The underlying bedrock of the lake is largely composed of several types of limestone, some of which have relatively high manganese content (Kentucky Geological Survey, 2008).

More pronounced differences were seen in dissolved methane concentrations (fig. 4A). It was relatively high near the bottom of the lake, being approximately two orders of magnitude higher than near the lake's surface. The trend was the same for ammonium (fig. 4B), the concentrations of which increased from $0.3 \mu\text{g L}^{-1}$ at the surface of the lake to $1.67 \mu\text{g L}^{-1}$ at the bottom of the lake. These differences are likely due to summer stratification of the lake which prevents vertical mixing and impedes the loss of gaseous species.

WASTE LAGOON SAMPLES

We attempted to take samples from the waste lagoon at 0.3- and 0.9-cm depths as well as in the sludge layer. These latter samples could not be taken, however, due to the ball check valve's relatively narrow bore becoming plugged with hair and other coarse material. In the case of the two other depths, there was a slight tendency for all chemical parameters to occur at higher levels at 0.9 m. The differences were not pronounced, however. For this reason, data presented here are the mean for samples collected at the two depths combined.

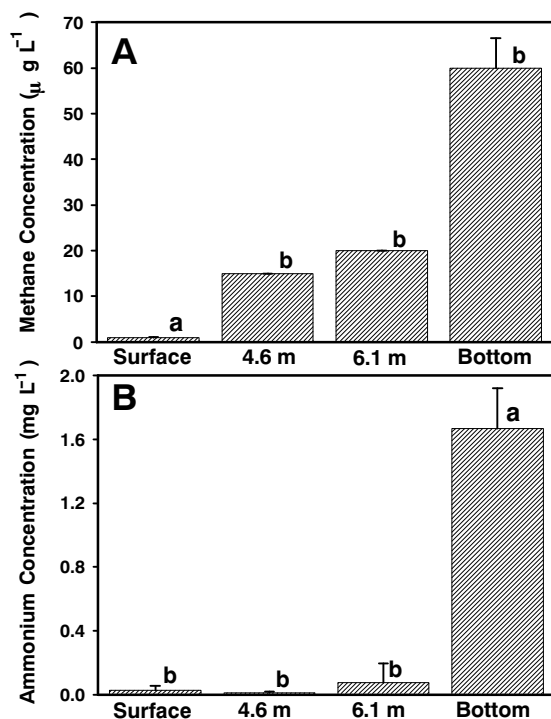


Figure 4. Dissolved methane (A) and ammonium concentrations (B) from Barren River Lake reservoir late summer of 2008. Data represent the means of three determinations \pm standard deviation. Within each graph, bars labeled with the same letter are not significantly different by a LSD test at $\alpha = 0.05$.

From early spring to mid-summer, the levels of ammonium more or less steadily declined (fig. 5A). This was expected since ammonia losses from lagoons are well known to increase in warm weather (Aneja et al., 2001). Methane concentrations showed a slight tendency to decline as the year progressed but this difference was not pronounced. Since methane production is greatly enhanced in warm seasons (DeSutter and Ham, 2005), this decline was likely due to decreased gas solubility as the lagoon warmed.

Levels of the malodorous compounds p-cresol and skatole decreased dramatically during the months of May and June and p-cresol was undetectable by late July (fig. 5B). This has been well documented and could be ascribed to the catabolic activities of diverse groups of microorganisms such as methanogens, sulfate reducing bacteria, and purple sulfur bacteria (Cappenberg, 1975; Gu and Berry, 1991; Boopathy, 1997; Do et al., 2003). Although the concentrations of the malodorants may have been underestimated due to the silicone tubing in the sampling vessels as described below, we were able to document relative changes in these compounds concentrations over an extended period.

Few other parameters varied as markedly during the study period, however, with the exception of COD and suspended solids. COD declined from about $2,730 \text{ mg L}^{-1}$ in late March to 120 mg L^{-1} in late July whereas TSS declined from $1,391$ to 216 mg L^{-1} . Again, enhanced catabolic activities of microbial consortia during the warm season are the likely cause of these improvements.

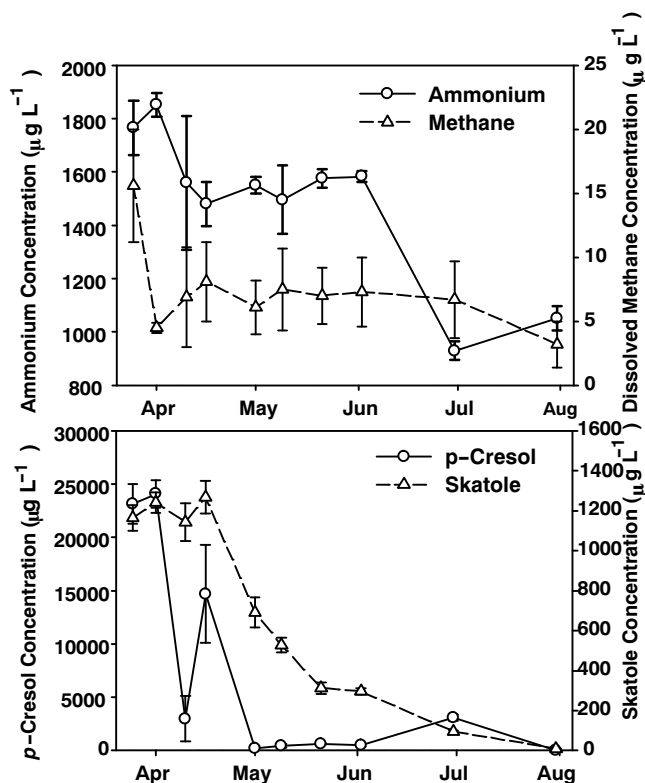


Figure 5. Ammonium and methane (A) and p-cresol and skatole concentrations (B) from a swine waste lagoon. Data represent the mean of 10 determinations \pm standard deviations from 5 samplings each at depths of 0.3 and 0.9 m.

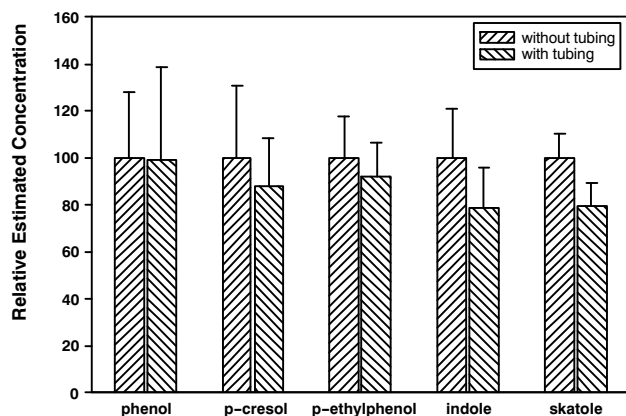


Figure 6. Apparent concentrations of odor compounds measured in sampling jars with and without added silicone tubing. Data represent the mean of six determinations \pm standard deviation.

EFFECT OF SILICONE TUBING ON ODOR COMPOUND ANALYSIS

Results of odor analyses from jars with and without added silicone tubing, as employed for dissolved gas analysis, are presented in figure 6. For clarity of presentation, concentrations were normalized to the highest measured concentration normalized to 100.

For the most polar compound measured, phenol, the measured concentrations were virtually identical in jars with or without added silicone tubing. For all other compounds, however, apparent concentration was lowered in the jars that contained silicone tubing and for the least polar compound measured, skatole, apparent concentration was lowered by about 20%. This finding shows that care must be taken when using this apparatus for the measurement of dissolved organic compounds in water. Either the target analytes must have sufficient polarity or the size of the sampling vessel relative to the tubing must be sufficiently large so as not to deplete dissolved analytes in the water sample.

CONCLUSION

We have demonstrated a device which facilitates the collection of water samples at well-defined depths and without loss of dissolved gas or atmospheric contamination. In the configuration used here, the bottles were submerged and water samples were taken at the jar's inlet without passing through the peristaltic tubing. A more convenient way of sampling, perhaps, would entail lowering the peristaltic tubing to a desired depth and switching sampling jars above the water surface. In addition, a suitable screening device and/or a wider bore check valve may allow for the collection of more viscous samples with coarser particle sizes such as in sludge layers.

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REFERENCES

- Aneja, V. P., B. P. Malik, Q. Tong, D. Kang, and J. H. Overton. 2001. Measurement and modelling of ammonia emissions at waste treatment lagoon-atmospheric interface. *Water Air Soil Pollut. Focus* 1(5-6): 177-188.
- APHA. 1998. *Standard Methods for the Examination of Water and Wastewater*. 20th ed. Washington, D.C.: American Public Health Association, American Water Works Association, and Water Environment Federation.
- Boopathy, R. 1997. Anaerobic phenol degradation by microorganisms of swine manure. *Curr. Microbiol.* 35(1): 64-67.
- Cappenberg, T. E. 1975. A study of mixed continuous cultures of sulfate-reducing and methane-producing bacteria. *Microb. Ecol.* 2(1): 60-72.
- Cey, B. D., G. B. Hudson, J. Moran, and B. Scanlon. 2008. Impact of artificial recharge on dissolved noble gases in groundwater in California. *Environ. Sci. Tech.* 42(4): 1017-1023.
- DeSutter, T. M., and J. M. Ham. 2005. Lagoon-biogas emissions and carbon balance estimates of a swine production facility. *J. Environ. Qual.* 34(1): 198-206.
- Do, Y. S., T. M. Schmidt, J. A. Zahn, E. S. Boyd, A. de la Mora, and A. A. DiSpirito. 2003. Role of *Rhodobacter* sp. strain PS9, a purple nonsulfur photosynthetic bacterium isolated from an anaerobic swine waste lagoon, in odor remediation. *Appl. Environ. Microbiol.* 69(3): 1710-1720.
- Gu, J.-D., and D. F. Berry. 1991. Degradation of substituted indoles by an indole-degrading methanogenic consortium. *Appl. Environ. Microbiol.* 57(9): 2622-2627.
- Holter, P. 1990. Sampling air from dung pats by silicone rubber diffusion chambers. *Soil Biol. Biochem.* 2(7): 995-997.
- Howard, P. H., and W. H. Meylan. 1997. *Handbook of Physical Properties of Organic Chemicals*. Boca Raton, Fla.: Chemical Rubber Corporation Press.
- Jacinte, P.-A., and W. A. Dick. 1996. Use of silicone tubing to sample nitrous oxide in the soil atmosphere. *Soil Biol. Biochem.* 28(6): 721-726.
- Jacinte, P.-A., and P. M. Groffman. 2001. Silicone rubber sampler to measure dissolved gases in saturated soils and water. *Soil Biol. Biochem.* 33(7-8): 907-912.
- Kentucky Geological Survey. 2008. Groundwater resources of Barren County. Available at: www.uky.edu/KGS/water/library/gwatlas/Barren/Geology.htm. Accessed 23 November 2009.
- Liu, Z., G. Stewart, J. K. Cochran, C. Lee, R. A. Armstrong, D. J. Hirschberg, B. Gasser, and J.-C. Miquel. 2005. Why do POC concentrations measured using Niskin bottle collections sometimes differ from those using in-situ pumps? *Deep-Sea Research I* 52(7): 1324-1344.
- Spaulding, B. P., and D. B. Watson. 2006. Measurement of dissolved H_2 , O_2 , and CO_2 in groundwater using passive samplers for gas chromatographic analyses. *Environ. Sci. Tech.* 40(24): 7861-7867.
- Strady, E., C. Pohl, E. V. Yakushev, S. Krüger, and U. Hennings. 2008. PUMP-CTD-System for trace metal sampling with a high vertical resolution. A test in the Gotland Basin, Baltic Sea. *Chemosphere* 70(7): 1309-1319.
- Warren, B. A. 2008. Nansen-bottle stations at the Woods Hole Oceanographic Institution. *Deep-Sea Res Pt I* 55(4): 375-395.
- Worthington, L. V. 1982. Loss of dissolved oxygen in Nansen bottle samples from the deep Atlantic Ocean. *Deep-Sea Research, Part A: Oceanographic Research Papers* 29(10): 1259-1266.